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# CERTIFICATE

This certificate is issued in support of an application for Patent registration in a country outside New Zealand pursuant to the Patents Act 1953 and the Regulations thereunder.

I hereby certify that annexed is a true copy of the Provisional Specification as filed on 11 July 2002 with an application for Letters Patent number 520114 made by VICTORIA LINK LTD and MASSEY UNIVERSITY.

Dated 31 July 2003.

Neville Harris

Neville Harris
Commissioner of Patents

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**LD OF THE INVENTION**

The present invention relates to nuclear magnetic resonance spectroscopy apparatus. More particularly but not exclusively it relates to one-sided access nuclear magnetic resonance spectroscopy apparatus.

**BACKGROUND TO THE INVENTION**

This invention relates to the field of nuclear magnetic resonance (NMR) spectroscopic devices. NMR spectroscopy is an analytical and diagnostic technique that can be used for the structural and quantitative analysis of a compound in a mixture. NMR is based on the nuclear magnetic properties of certain elements and isotopes of those elements. It is based on the principle that nuclei with a non-zero spin will have a magnetic dipole and therefore will interact with electromagnetic (EM) radiation.

The presence or absence of a spin and the nature of this spin is expressed in terms of the spin quantum number of the nucleus, which may either be 0, ½ or multiples of ½.

In a uniform magnetic field a nucleus having a spin quantum number of ½ may assume two orientations relative to the applied magnetic field. The two orientations have different energies so that it is possible to induce a nuclear transition by the application of electromagnetic radiation of the appropriate frequency. This transition is resonance. Resonance arises when the correct combination of magnetic field strength and exciting frequency characteristics of the nuclei of interest are applied.

After resonance is achieved the NMR instrument records a signal, the signal being a function of the nature and amount of a compound of the test sample as well as nuclear magnetic relaxation considerations.

An NMR spectrometer generally comprises one or more magnets producing a strong homogenous field within a test region. The size and complexity of NMR spectrometers are largely a function of the magnetic field requirements.

Conventional NMR requires a laboratory electromagnet, or superconducting magnet. The spectroscopic information is obtained by using uniform magnetic fields and thus the technique is inherently invasive as the field uniformity is restricted to small volumes and materials must be placed inside the magnet system.

An alternative design is the "inside out" NMR which uses open magnet designs for measurements in the field without sample size restrictions. However a disadvantage of

a design is reduced sensitivity and lack of resolution and the field is less uniform than in such a magnetic configuration.

A development beyond the use of inside out NMR relates to the development of mobile NMR devices which have been developed for analysis of many things including oil wells, water reservoirs, plant growth and life cycles and moisture detection (for example in wood or concrete).

There are a number of difficulties associates with the development of small scale inside NMR apparatus. These include:

1) the homogeneity of the magnetic field;
2) it is important to provide a magnet with the highest field possible;
3) such a strong magnetic field generally requires larger, heavier magnets, which increases the costs of the spectrometer;
4) with such a magnet configuration typically only the surface area of a subject can be analysed by the technique.

A number of parties have applied themselves to these difficulties in the development of small scale NMR apparatus.

US6,163,154, (Anderson et al), discusses the development of small scale NMR apparatus for the measurement of a patient's glucose levels. It employs a pair of opposed permanent magnets and a plurality of annual circular magnets which are cancelling magnets.

US6,081,116, (Wu et al), deals with NMR apparatus for geological applications and employs a plurality of cylindrical magnets to approximate a permanent ring magnet. This will reduce the cost of the use of a single ring magnet.

US5,959,454, (Westphal et al), deals with the magnet arrangement for an NMR tomography system for skin and surface examinations. This is a one sided NMR system having two ring magnets and a cylindrical magnet the locations being so as to impart a certain degree of uniformity.

A number of people have alternatively attempted to deal with the problem that in one sided NMR, often only the surface region of the sample is analysable due to magnetic field concerns.

US5,739,688, (Krieg), attempts to profile in the *z*-axis direction (into the sample), by employing a static magnetic field having a predetermined inhomogeneity in the z direction. It uses slices perpendicular to the direction of inhomogeneity (z axis) with

ating the apparatus by a pulse sequence with shortened measurement time. This allows for excitation of one slice independent of another, and overcomes relaxation disadvantages.

US5,126,674, (Miller et al), again deals with a one sided NMR apparatus and the technique of planar imaging. It creates an inhomogeneous magnetic field and the RF frequency selection excites only one "volume of interest" at a time. Again there is no need for relaxation as each is excited independently of the other.

US4,528,509, (Radda et al), and US4,710,713, (Strikman), both similarly deal with three dimension imaging via a homogenous field in the *z*-axis direction.

## OBJECT OF THE INVENTION

It is an object of the present invention to provide one-sided NMR apparatus which overcomes or at least ameliorates some of the abovementioned disadvantages; or which at least provides the public with a useful choice.

Other objects of the invention may become apparent from the following description which is given by way of example only.

## SUMMARY OF THE INVENTION

According to the first aspect of the invention there is provided **nuclear magnetic resonance apparatus** for one sided access investigations of a material, including or comprising a plurality of permanent magnets disposed in an array about an axis (hereafter for clarity purposes "longitudinal axis"), the arrangement and/or characteristics of the plurality of magnets being such so as to create a zone of homogeneous magnetic field at some location along the axis forward of the array (and into the material when provided).

Preferably each of the plurality of magnets is a cylindrical bar magnet, each having a proximal end at the front of the array, and a distal end at the rear of the array.

Preferably each of the plurality of magnets is substantially identical.

Preferably the plurality of magnets is disposed symmetrically about the longitudinal axis.

Preferably the proximal end of each of the plurality of magnets is tilted through an angle beta towards the longitudinal axis, such that the configuration of magnets is in a substantially symmetrical tapered arrangement, tapering towards the front of the array.

Preferably the magnets are as close together as is physically or reasonably possible.

Preferably the tapered arrangement is according to the expression:

$$R = r|\cos\beta|\sqrt{1+\frac{1}{\tan^2\frac{\pi}{N}\cos^2\beta}} + |l\sin\beta|$$

$$t = \sqrt{r^2+\left(\frac{l}{2}\right)^2}\max(|\cos(\beta-\phi)|,|\cos(\beta+\phi)|)$$

where

$\phi = \tan^{-1}(\frac{2r}{l})$

$N$ is the number of magnets used,

$r$ is the radius of the magnets

$l$ is the length of the magnets

$\beta$ is the 'cone angle'

$R$ is the 'ring radius'

$z$ is the longitudinal axis, the front of the array position substantially at $z = 0$

Preferably the nuclear magnetic resonance apparatus includes a secondary permanent magnet located along the longitudinal axis, centrally within the tapered arrangement.

Preferably the secondary magnet is a cylindrical bar magnet, preferably of substantially identical dimensions to each of the plurality of magnets.

Preferably the nuclear magnetic resonance apparatus is portable.

Preferably it provides investigations into a sample at up to 10cm.

Preferably the dimensions of the plurality of magnets and secondary magnet are radius 1.8cm and length 5cm

Preferably the number of primary magnets is 8.

Preferably the apparatus may be operated in such a fashion as to allow excitation of one volume $V_a$ of the material, being one of a plurality of volumes $V_1$ to $V_n$ existing as slices along the z-axis.

Preferably the apparatus may be operated to, following excitation of $V_a$ then allow excitation of a second volume $V_b$ being one of the plurality of volumes $V_1$ to $V_n$ substantially immediately after excitation of $V_a$.

According to a second aspect of the invention there is **provided a magnetic assembly for an NMR apparatus,** the assembly providing or to provide a substantially homogeneous magnetic field forward of the assembly for example, along for example a *z*-axis, said assembly having an array of magnets disposed about an axis such that similar poles of similar magnets obliquely angled to converge towards the axis at a region thereof which in use is to be more adjacent any sample to be subject to nuclear magnet resonances than is the case for the other poles of each magnet of the array.

Preferably the nature of the magnets and their relationship to the axis and any intended sample and/or the remainder of the apparatus as substantially as herein described.

According to a further aspect of the invention there is provided **a method of studying the magnetic resonance of a material** comprising or including the steps of:

a) employing the NMR apparatus as described above;
b) generating a sufficiently homogeneous magnetic field over a volume $V_a$ located at a location along the *z*-axis in the material thereby causing excitation of subject nuclei in the volume $V_a$;
c) detection of radio frequency emissions from the subject nuclei in the volume $V_a$.

Preferably the method may include subsequent to step c)

d) substantially immediately following excitation of volume $V_a$, causing excitation of subject nuclei in the volume $V_b$, wherein $V_b$ is a volume differing from $V_a$ only in its position along the *z*-axis
e) detection of radio frequency emissions from the subject nuclei in the volume $V_b$.

According to a further aspect of the invention there is provided **a magnetic assembly for an NMR apparatus,** the assembly providing a substantially homogeneous magnetic field forward of the assembly substantially as herein described and with reference to the accompanying drawings.

Where, in this specification the term "homogeneous magnetic field" is used, it is to be given the meaning a sufficiently homogeneous magnetic field so as to enable NMR excitation of a sufficient volume of sample and to provide an analysable NMR signal in that region.

Other aspects of the invention may become apparent from the following description which is given by way of example only and with reference to the accompanying drawings.

Where in the foregoing description reference has been made to elements or integers having known equivalents, then such equivalents are included as if they were individually set forth.

Although the invention has been described by way of example and with reference to particular embodiments, it is to be understood that modifications and/or improvements may be made without departing from the scope or spirit of the invention.

## BRIEF DESCRIPTION OF THE DRAWINGS

The invention will now be described by way of example only and with reference to the drawings in which:

Figure 1: Illustrates the approximation of a cylindrical ring magnet by an array of cylindrical bar magnets.

Figure 2: illustrates the array of Figure 1 with a central magnet to provide greater field homogeneity.

Figure 3: illustrates the field produced by the array of Figure 2.

Figure 4a: illustrates tilting of the outside magnets (cross sectional view).

Figure 4b: illustrates the field produced by the array of Figure 4a.

Figure 5a: illustrates the use of a central magnet in the array of Figure 4a (cross sectional view).

Figure 5b: illustrates the arrangement of Figure 5a.

Figure 6: illustrates the field produced by the arrays of Figure 5a and 5b.

Figure 7: illustrates preferred array of the example that will give a homogenous region at a depth of 5.25cm with a field strength of 0.0127T.

Figure 8: magnetic field at distance Z.

Figure 9: strength of uniform region.

Figure 10: position of uniform region.

## DETAILED DESCRIPTION OF THE INVENTION

We have a number of objectives in the development of our system. Firstly we wish to reduce the cost of employing an expensive permanent magnet in portable NMR

ratus applications and secondly we wish to use our magnetic arrangement to study a substrate in the region below the surface. We achieve this by a unique arrangement of cylindrical magnets. As will be discussed in detail below, this arrangement involves the use of a plurality of cylindrical magnets, arranged to approximate a single ring magnet but differing crucially in that the magnets are tilted to provide to a cone shaped configuration.

**Magnet Array**

The starting point for our magnetic arrangement or array involves a replacement of a single ring magnet with a series of cylindrical magnets. These provide an approximation to the ring magnet and have the important advantage that standard "off the shelf" cylindrical magnet can be used. This is a far cheaper way of approaching the problem.

Figure 1 is a schematic illustrating the use of plurality of cylindrical magnets to approximate a single permanent ring magnet.

To provide a good approximation of a solid ring, the individual magnets need to be as close as possible.

**Homogeneity**

There are a number of considerations in regard to obtaining a homogeneous field.

The field produced from a small array of magnets will never be perfectly homogeneous, so there needs to be a way of characterising the field's homogeneity. This can be done by looking at the Taylor expansion of the field at the point $a$.

$$B_{Taylor}(z)=c_0+c_1(z-a)+c_2(z-a)^2+c_3(z-a)^3+c_4(z-a)^4+\ldots$$

$$c_n=\frac{B^{(n)}(a)}{n!}$$

where $B^{(n)}$ is the $n$th derivative of $B$.

The expression $B_{\mathrm{Taylor}}(z)$ describes the field in a region around the point $a$. The $c_0$ coefficient gives the strength of the field and the coefficients $c_1,c_2,\ldots$ describe the inhomogeneity in the region. The first non-zero term will always be the dominant one that destroys the homogeneity. By manipulating the source of the field so that the first few coefficients are zero, a quasi-uniform field will result.

The well-known configuration of 'Helmholtz coils' does exactly that. Due to symmetry, the odd coefficients are zero but also the second order term. This leaves us with the first non-zero term $c_4$ so we have 'fourth order' field.

As discussed above, to generate a remote field of sufficient homogeneity we use a series of cylindrical magnets arranged in a ring with a single magnet in the middle as illustrated in Figure 2. The dimensions of magnets the make up the ring, and the number of magnets can be varied. The dimensions of the middle magnet can also be varied, but the position is determined by the `homogeneity condition', that is, there is one specific placement of the central magnet which results in there being one point on the $z$-axis where the 1st and 2nd derivatives are zero.

**Example Homogeneity Calculation**

For example, we choose 8 magnets with magnetisation 1.20 T, length 4.00cm, radius 1.00cm and arranging them axially in a cylinder about the $z$-axis so they are as close as possible. If we place a central magnet of the same dimensions in the middle, the homogeneity condition if the central magnet is placed at $z$ = -2.62cm. This gives a depth of 0.91cm and a strength of 0.137 T, as illustrated in Figure 3. Figure 3 is a graph illustrating the homogeneous region obtained from a ring with a central magnet as shown in Figure 2.

**Arrangement of the Magnets in the Array**

A further advantage of the use of a plurality of cylindrical magnets is that these can be angled inwards or outwards to give a distinctive cone shape. This is the second important feature of our apparatus.

Figure 4 is a schematic illustrating the tilting to provide a cone shape. The outer magnets that make up the ring are tilted by an angle $\beta$ to give the "cone shape".

**Tilted Ring design**

The strength and depth achieved by a ring will depend on the size of the magnets and the angle at which they are tilted. Greater depths are achieved when the magnets are tilted outwards, i.e. $\beta$ is positive.

It is useful to describe the size of array in a dimensionless form using the radius, $r$, as the scaling parameter. Figures 9 and 10 show the strength of the uniform region and the scaled depth of this region for different angles and different scaled lengths.

It is apparent that as the angle b increases, the strength goes down and the depth goes up and appears to be a direct trade off. Angles between .33 and .82 appear suitable. The most favourable length to radius ratio is not immediately clear, values between 2 and 4 contain a maximum in Figure 9 through most angles and seem the best choice.

The dimensions stated in the case study are shown as a circle in both graphs.

While not essential, it is preferable to construct the magnet ring in such a way that the outside magnets are as close as they can be. Because the 'depth' refers to the distance from the homogeneous region to the magnet, it makes sense to place the magnet array so that the top of the magnets are at $z = 0$. Both of these conditions are met if the magnets are arranged as illustrated in Figure 4a.

With reference to Figure 4a, to ensure that the top of the ring is at $z = 0$ and that the magnets are as close as they can be, $R$ and $t$ are calculated as follows:

$$R = r\left|\cos\beta\right|\sqrt{1+\frac{1}{\tan^2\frac{\pi}{N}\cos^2\beta}}+\left|l\sin\beta\right|$$

$$t = \sqrt{r^2+\left(\frac{l}{2}\right)^2}\,\max\left(\left|\cos(\beta-\phi)\right|,\left|\cos(\beta+\phi)\right|\right)$$

where

$$\phi = \tan^{-1}\left(\frac{2r}{l}\right)$$

$N$ is the number of magnets used,

$r$ is the radius of the magnets

$l$ is the length of the magnets

$\beta$ is the 'cone angle'

$R$ is the 'ring radius'

Figure 4b illustrates the resultant $z$-axis field profile.

Figures 5a and 5b illustrates the cone shaped array with a central magnet. The central magnet is placed so that there is a homogeneous region at some $z$. Figure 6 illustrates the $z$-axis field profile for such an arrangement.

For every ring configuration there is a position for the central magnet that will give a homogeneous region as described above. The other parameters, number of magnets, length and radius etc can be adjusted to optimise the depth of the homogenous region or the strength.

Therefore, in general the design of the invention involves placing a number of similar magnets in a ring at some angle ($\beta$), and the placing of another magnet is placed in the middle so that there is one point on the $z$-axis where the 1st and 2nd derivative of the field is zero. This gives a homogenous region.

**Design Example**

Various designs involve magnets of different sizes, rings of various numbers of magnets and cones with various angles. All of these will produce a homogeneous region of a particular field strength and at a particular depth. For an one sided access-NMR application, a field strength of 0.01 T might be required. This can be realised with an array of magnets as shown below:

$r = 1.80\text{cm}$

$l = 5.00\text{cm}$

$\beta = 37.2°$

$N = 8$

This gives

$R = 6.09\text{cm}$

$t = 3.05\text{cm}$

and the central magnet (of the same dimensions) at z = -3.27cm

The homogenous region is at $z = 5.25\text{cm}$ with a field strength 0.0127 T. This is illustrated in Figure 7. This shows a magnet array that will provide a homogeneous region at a depth of 5.25cm with a field strength of 0.0127T. The field is illustrated in Figure 8.

**Depth Considerations:**

The depth of the subject area, into a sample, that can be studied depends upon (assuming a constant number of magnets) the angle, $\beta$, the length to radius ratio and the required field strength.

With reference to the above example, if $\beta$ was kept constant and the length to radius ratio was increased, the depth would also increase, as shown in figure 10. It is important to note that the strength of the $B$ field will start to
decrease as the length to radius ratio gets larger than about 2.7, as shown in figure 11.

In practice, the depths we will be dealing with are up to 10cm. In general, if the angle and the ratio are fixed, the depth will scale with the size of the magnets, i.e. double the dimensions of the magnets, double the depth.

**Excitation of Separate "Slices" or "Volumes"**

The direct relationship between magnetic field intensity and NMR frequency means that the field profile associated with the magnet configurations described here necessarily corresponds to a frequency profile for the nuclear spins being excited in the NMR measurement. In particular, the range of frequencies present in the excitation pulse (the pulse bandwidth) will determine the spatial range of spins excited in the region of nearly uniform magnetic field. This bandwidth is in turn limited by the rf power available in the transmitter. Thus the largest region of spins, and hence the strongest signal will be obtained, when the rf power is at a maximum.

The relationship between rf pulse power and field uniformity thus determines the spatial extent of the region of sample excited in the NMR measurement and also the size of the signal measured and hence the intrinsic sensitivity of the experiment.

Repetition of the rf excitation pulse, and hence the sensitivity advantage which comes from repeating and adding many independently acquired signals (signal averaging) is limited by the need for the nuclear spins to relax back to thermal equilibrium, a process which takes on the order of 0.1 s to 10 s, depending on the sample.

To further increase the signal sensitivity or to further extend the region of sample from which the signal is acquired, the technique of successively switching the transmitter and receiver frequencies on successive excitations and acquisitions will be effective. With each successive excitation, the rf excitation frequency will be changed so as to excite a contiguous slice, cyclically stepping the region of spins excited through adjacent slices. Provided that the total time allowed before repeating excitation on the same slice is sufficient for relaxation, this process may be take place rapidly with successive slices being examined in times much less than the relaxation time. In this way the fundamental

iency of the measurement is improved. Furthermore by suitable multiplexing, information from different spatial regions may be separated to give spatial profiling.

This switching technique depends on switching the tuning frequency of the rf coils, a technique which depends on electronic switching between differing tuning elements (capacitors).

**Applications:**

The NMR apparatus of the invention has a large number of applications. The preferred embodiment employs a number of "off the shelf" cylindrical magnets which can be any of a number of proportions. It is envisaged the most common of these will be smaller magnets to provide a portable NMR Probe for various applications (however, the invention is not restricted to portable probes).

All applications will include the use of such apparatus to study liquid phases (whether in a solid phase, or within other liquid phases). Such applications include moisture studies. Specific examples are:

- moisture content of soil;
- moisture levels in buildings;
- moisture content of timber and logs;
- location of knots and defects in timber and logs;
- drug detection in humans;
- in-vivo spectroscopy on humans and animals;
- moisture analysis of packaged food.

One particular example is the application of the probe to studies of the curing of concrete as outlined below.

**Example:**

Concrete is a mixture of water, cement, sand and gravel. The water is contained in three different states, chemically bound, capillary bound and free water. During the curing process, the relative fraction of these three states changes as water evaporates from the surface. The moisture content of the concrete gives an indication of its strength and readiness to accept floor coverings. Presently there is no reliable way of measuring this.

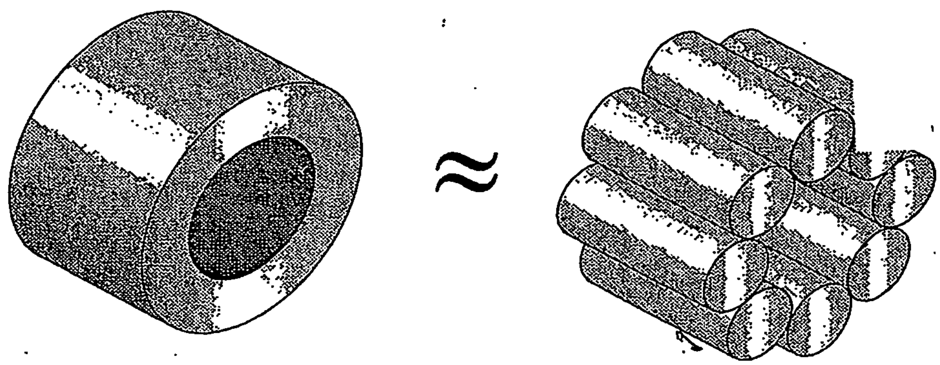
The one sided access NMR probe of the invention provides a convenient way of measuring the moisture. One part of such a probe is achieving a homogenous magnetic field $B_0$ at a useful depth of approximately 5cm.

Where in the foregoing description reference has been made to elements or integers having known equivalents, then such equivalents are included as if they were individually set forth.

Although the invention has been described by way of example and with reference to particular embodiments, it is to be understood that modifications and/or improvements may be made without departing from the scope or spirit of the invention.

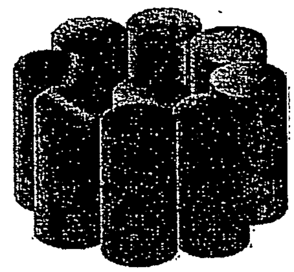
DATED THIS 11th DAY OF July 2002
AJ PARK
PER
AGENTS FOR THE APPLICANT

FIGURE 1

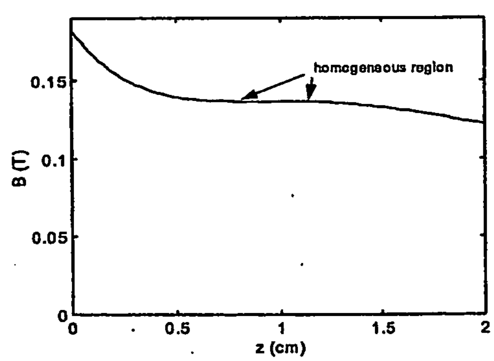


## FIGURE 2

**Field produced from simple magnet array**



## FIGURE 3



## FIGURE 4a

**Design of Ring**

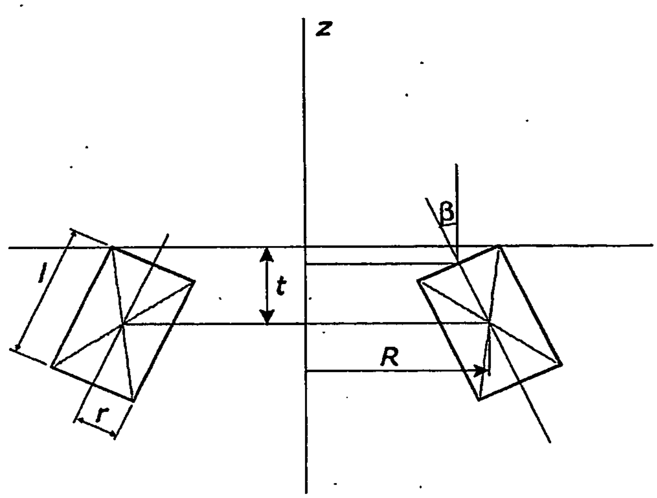


**FIGURE 4b**

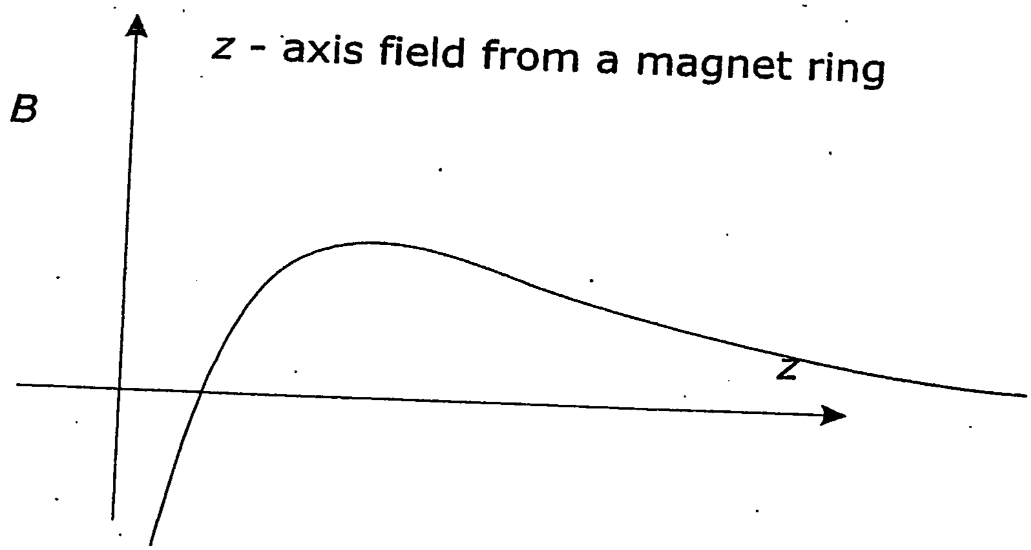


**FIGURE 5a**

**Magnet ring and central magnet.**

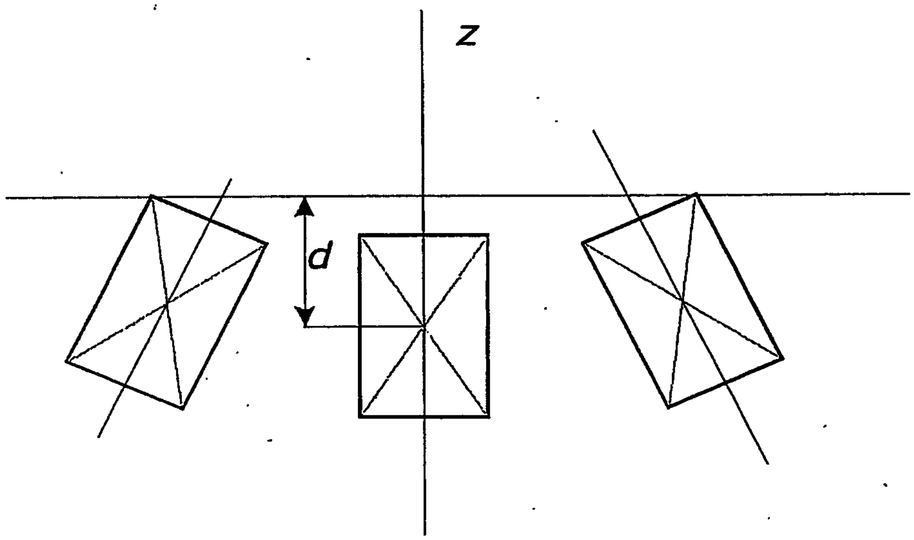


FIGURE 5b

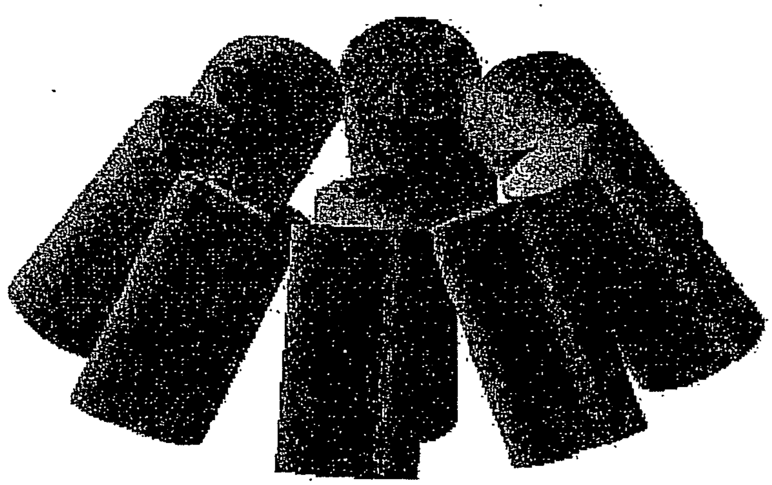
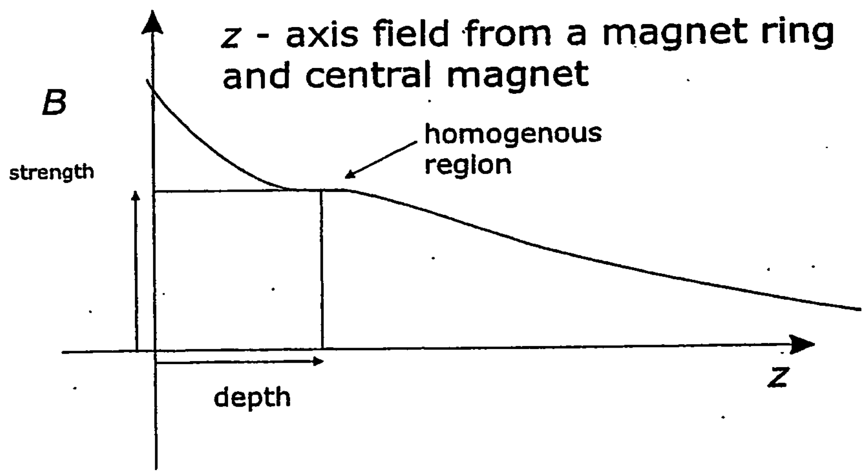


**FIGURE 6**



z - axis field from a magnet ring and central magnet
B
strength
homogenous region
depth
z

**FIGURE 7**

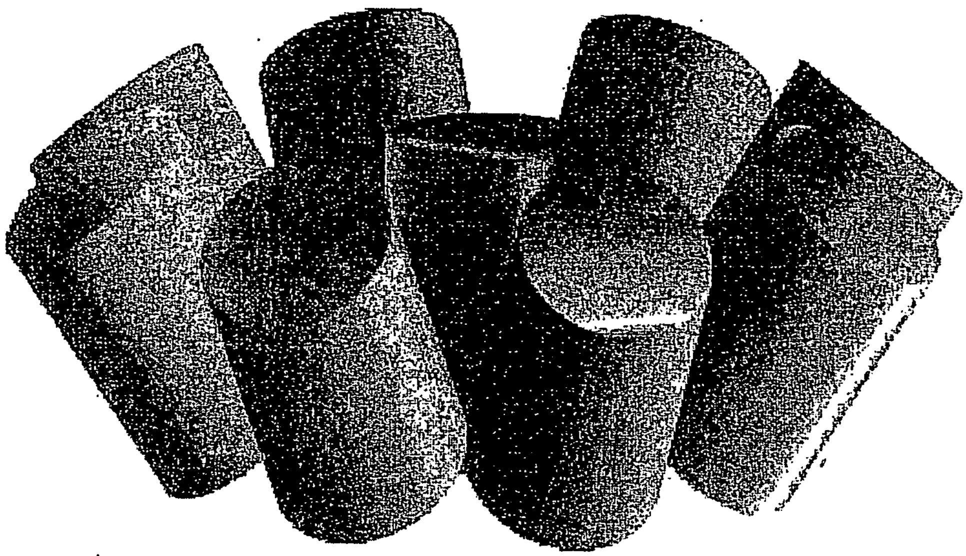
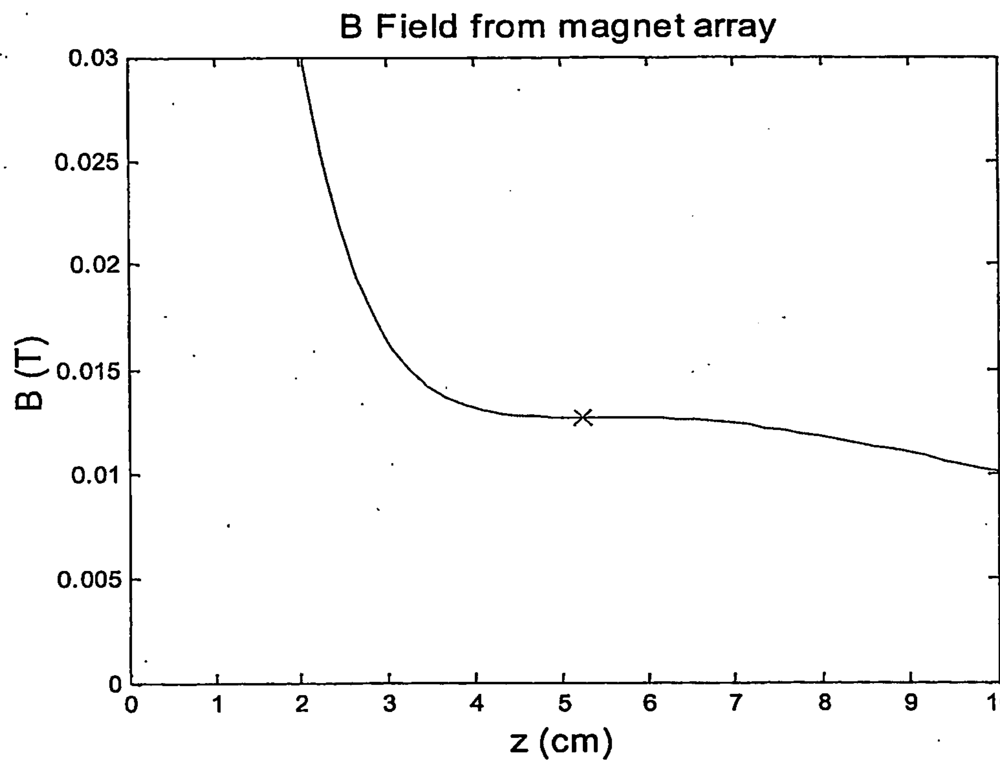
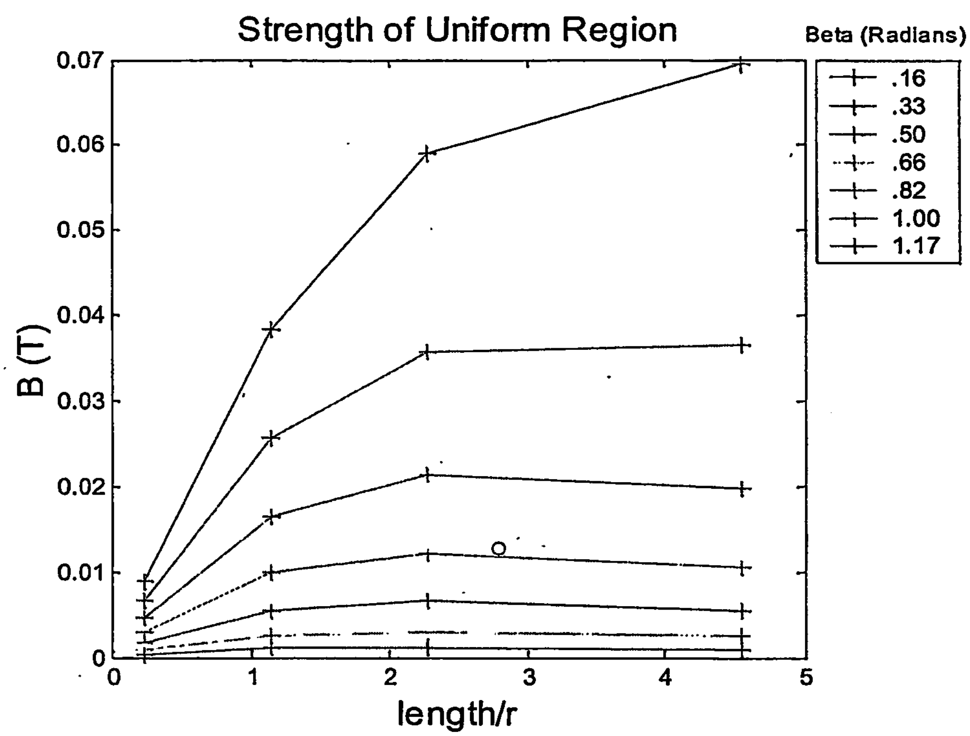


**FIGURE 8**




**The red cross shows the point at which the uniform region is centred around.**

**FIGURE 9**




**Strength of uniform region. As the angle β gets larger, the strength of the region decreases. At most angles the strength decreases slightly with a length/r ration of above approximately 2.5.**

520114



NEW ZEALAND

PATENTS ACT, 1953

**PROVISIONAL SPECIFICATION**

"NMR APPARATUS"

We, VICTORIA LINK LIMITED, a company duly incorporated under the laws of New Zealand of 15 Mount Street, Kelburn, Wellington, New Zealand and MASSEY UNIVERSITY a body corporate established under the Massey University Act 1963 and Education Amendment Act 1990 of Palmerston North, New Zealand, do hereby declare this invention to be described in the following statement:

Intellectual Property Office of N.Z.

11 JUL 2002

RECEIVED